

Supporting Information Available:

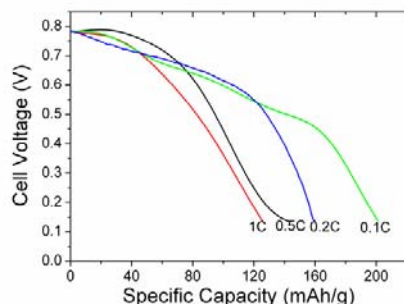


Figure S1 Discharge behavior of Al/I₂-C cell at different discharge rates.

The TiO₂ (P25, Degussa, average particle size 21nm) porous film was deposited on F-doped tin oxide (FTO) conducting glass by a screen-printing technique. The thickness of the TiO₂ film was about 10 μ m. Dye (RuL₂(NCS)₂·2H₂O, L=2,2'-bipyridyl-4,4'-dicarboxylic acid, Solaronix) adsorption was performed by soaking the TiO₂ films in the dye ethanol solution (3×10^{-4} mol/L). Electrolytes were dropped on the dye-anchored TiO₂ films and then a sputtered platinum-coated counter-electrode was clipped firmly with the TiO₂/dye/electrolyte glass plate. A mask with a window of 0.15 cm² was also clipped on the TiO₂ side to define the active area of the cells.

The cells were illuminated by an Oriel solar simulator (91192) under AM 1.5 (100 mWcm⁻²) irradiation. The incident light intensity was measured by a radiant power/energy meter (Oriel 70260). The current density-voltage (*I*-*V*) characteristics of the cells were recorded by a potentiostat/galvanostat (PAR, Model 263A).

The influence of iodine concentration on the performance of aluminum iodide base electrolytes in ethanol is shown in Figure S2. The highest energy conversion efficiency was achieved when the ratio of I₂/I⁻ was 1:10.

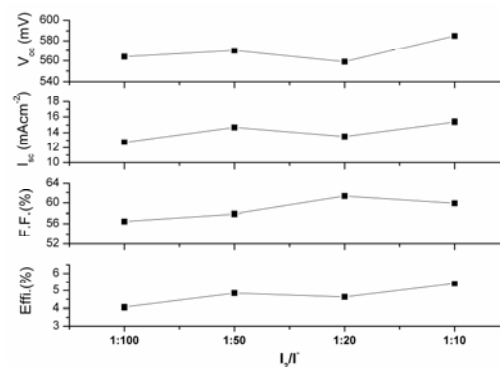


Figure S2 The DSSC parameters variations with the ratio of I₂/I⁻ in the AlI₃ based electrolyte in ethanol. [TBP] = 0.6 M, all the data were measure at AM 1.5, 100 mWcm⁻².

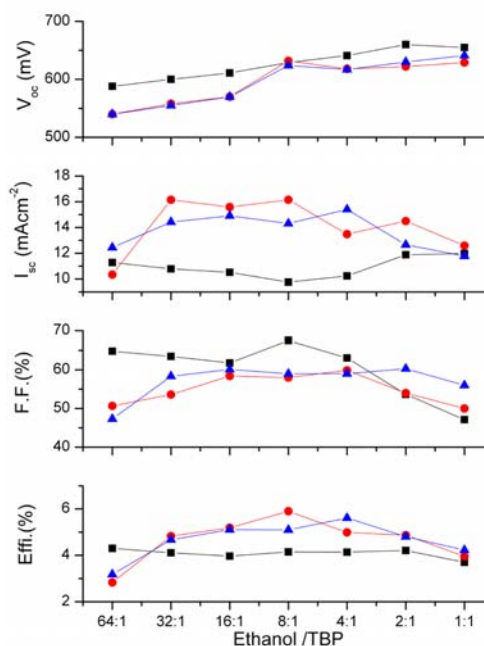


Figure S3 The DSSC parameters variations with the ratio of ethano/TBP (v/v). red: *in-situ* AlI₃ (electrolyte A), blue: commercial AlI₃ (electrolyte B), Black: LiI (electrolyte C). I₂/I⁻ = 1:10, all the data were measure at AM 1.5, 100 mWcm⁻².

The influence of the concentration of 4-*tert*-butylpyridine (TBP) is investigated by varying the ratio of ethanol/TBP. As shown from Figure S3, for electrolyte A and B, the variations of open-circuit voltage (*V*_{oc}), short-circuit photocurrent density (*I*_{sc}), FF

and overall energy conversion efficiency (η) show almost same trends, which indicates the *in-situ* AlI_3 based electrolyte's performance is same as or better than that of the commercial AlI_3 based electrolyte. Moreover, by this *in-situ* preparation method, we can prevent the hydrolysis of AlI_3 and avoid using very expensive anhydrous commercial AlI_3 . Also shown in Figure S3 is the performance of electrolyte C (LiI based electrolyte). Except the higher V_{oc} , the overall performance of LiI based electrolyte is inferior to aluminum iodide based electrolytes.

The following materials are supplied to demonstrate the chemical state of AlI_3 in ethanol.

AlI_3 has different state in different solvents.¹ It can exist as dissociated ions, or as dimmer molecules, or possibly as AlI_4^- ions, like the case of molten salts.^{2a} We compared the chemical state of AlI_3 in three different systems to clarify this point: (1) AlI_3 in ethanol at different concentrations (2) AlI_3 in n-hexane at different concentrations; (3) AlI_3 plus LiI in ethanol at different concentrations. The last system should be beneficial for the formation of AlI_4^- if it does exist.

In order to understand the chemical state of AlI_3 in different systems, we employed UV-Vis spectroscopy, FT-Raman spectroscopy, Secondary Ion Mass Spectrometry (SIMS) and conductivity measurements to characterize these solutions. UV-vis spectroscopy was employed to show the state of I^- and I_3^- ions. FT-Raman spectroscopy was used to check the existence of AlI_4^- ions and Al_2I_6 dimmers. SIMS (Cs^+ ion being the incident ion beam) was for checking the species of ions in an AlI_3 ethanol solution. Conductivity measurement is also helpful to understand the state of free ions in the solution. If AlI_3 in ethanol exists as dimmer mainly, the ionic conductivity should be very low, if it is dissociated, the solution should have respectable ionic conductivity. If AlI_4^- is formed preferably in the ethanol solution of AlI_3 and LiI instead of dissociated individual ions, Li^+ , Al^{3+} , I^- , the conductivity of AlI_4^- forming solution should be much less than that of a solution with dissociated AlI_3

and LiI since the free ions concentration and mobility are smaller in the former.

The following is the experimental results of the above mentioned methods.

(1) UV-vis spectroscopy results

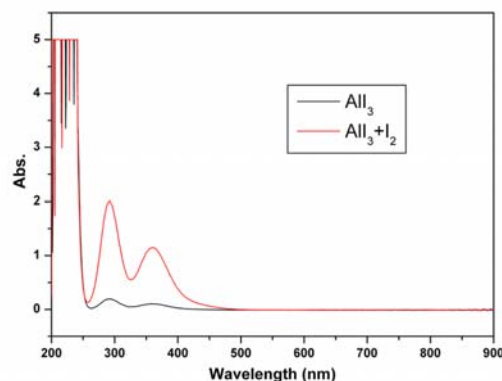


Figure S4 UV-vis spectra of the AlI_3 ethanol solution (black line) and the AlI_3 and I_2 ethanol solution (red line).

UV-vis spectroscopy was used to investigate the state of iodide in the solutions. The spectra were recorded by a UV-visible spectrophotometer (Shimadzu, UV-2550). Figure S4 shows the UV-vis spectra of AlI_3 ethanol solution (Solution 1, black line) and AlI_3 ethanol solution with addition of a small amount of I_2 (Solution 2, red line). In Solution 1, the concentration of AlI_3 was 2.5×10^{-3} M. The intense absorption of Solution 1 at about 220 nm can be assigned to I^- , whereas the very weak absorptions at 290 nm and 360 nm can be assigned to I_3^- .³ The existence of I_3^- in the Solution 1 can be ascribed to the oxidization of I^- by air during the sample preparation and testing. The spectrum indicates that, in Solution 1, AlI_3 could be dissociated and I^- exists as free ions. In Solution 2, $[\text{AlI}_3]$ was 2.5×10^{-3} M and $[\text{I}_2]$ was 4×10^{-5} M. The much stronger absorptions of I_3^- at 290 nm and 360 nm suggest the increased concentration of I_3^- .³ It can be inferred from Figure S4 that AlI_3 is dissociated in ethanol and I^-/I_3^- acts as a redox couple in the iodine-added AlI_3 electrolyte. The same phenomena can be observed in the LiI/ I_2 ethanol system.³

In order to clearly demonstrate the UV-vis spectra in the low wavelength range (< 300 nm), dilute solutions were prepared and the UV-vis spectra were recorded.

The UV-vis spectra of AlI_3 (0.05 mM and 0.15 mM) in n-hexane, AlI_3 (0.05 mM) in ethanol and LiI (0.15 mM) in ethanol are shown in Figure S5. In the ethanol solutions of AlI_3 (0.05 mM), an absorption peak at about 220 nm is observed while in the ethanol solutions of LiI (0.15 mM), an absorption peak at the same band is observed, which is assigned to I^- ions.³ Therefore, I^- anions exist in the dilute ethanol solutions of AlI_3 . In the n-hexane solution of AlI_3 (0.05 mM), there was no absorption peak at 220 nm (Figure S5). Even when the concentration of AlI_3 in n-hexane was increase to 0.15 mM, the absorption peak at 220 nm also cannot be observed (Figure S5).

These observations indicated that I^- and I_3^- did exist in AlI_3 ethanol solution while no I^- and I_3^- anions could be detected out in the case of AlI_3 in n-hexane.

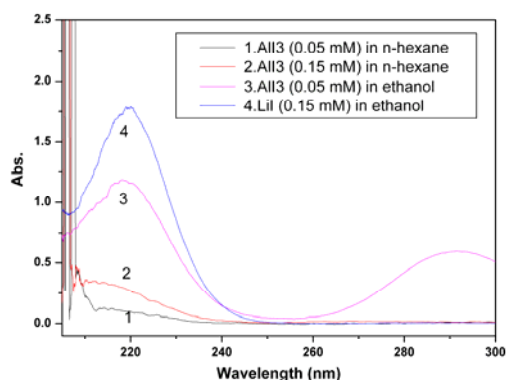
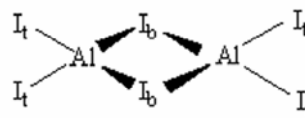


Figure S5 UV-vis spectra of AlI_3 and LiI in different solutions to show whether I^- ions absorption peak at 220 nm is present in these solutions.

(2) FT-Raman results

Solid-state AlI_3 exists as dimmers and can be written as $\text{I}_2\text{AlI}_2\text{AlI}_2$, where I_t is the terminal iodine atoms, I_b is the bridging iodine atoms (Scheme 1). The characteristic Raman frequency of the stretching vibration of Al-I_b in AlI_3 dimer molecule is 148 cm^{-1} .⁴



Scheme S1 The AlI_3 dimer

If AlI_3 exist as dimer molecules in a solvent, the Raman shift at 148 cm^{-1} will appear in the Raman spectrum. If AlI_3 is dissociated in a solvent, the Raman shift at 148 cm^{-1} will disappear. So we recorded the Raman spectra of AlI_3 (0.5 M) in n-hexane and in ethanol to detect the Al-I_b characteristic Raman shift.

The FT-Raman spectra (by a Bruker EQUINOX55) of n-hexane and AlI_3 (0.5M) n-hexane solution were recorded (Figure S6). When AlI_3 was dissolved in n-hexane, the peak at 148 cm^{-1} is still present and it could be assigned to the stretching vibration of Al-I_b .⁴ Moreover, in other Raman spectra range, the spectrum of n-hexane solution of AlI_3 was same to that of n-hexane and no change could be observed (data not shown). In contrast, when AlI_3 was dissolved in ethanol, no peak could be observed at 148 cm^{-1} (Figure S6), indicating that no AlI_3 dimer existed in the ethanol solution.

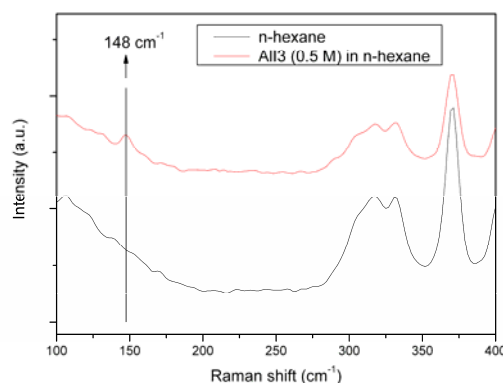


Figure S6 Raman spectra of n-hexane and n-hexane solution of AlI_3 (0.5 M) to show the characteristic Raman frequency of the stretching vibration AlI_3 dimer molecule at 148 cm^{-1} .

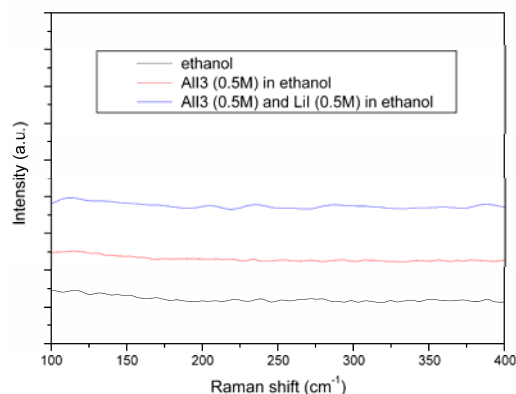


Figure S7 Raman spectra of ethanol and AlI_3 and LiI ethanol solutions to show that Raman frequency of the vibration of AlI_4^- at 146 cm^{-1} is absent.

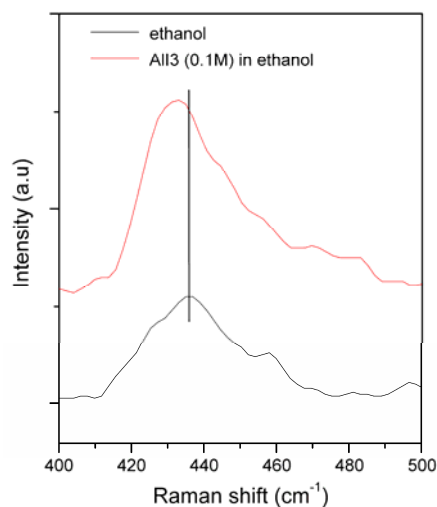
AlI_4^- was reported in an AlI_3/CsI molten salt system. The Raman vibration frequencies of AlI_4^- were reported to be 51 (m) , 82 (m) , 146 (s) and $336\text{ cm}^{-1}\text{ (w)}$.² (m, s and w stand for medium, strong, weak). As shown in Figure S7, the strong peak at 146 cm^{-1} is absent in the case of AlI_3 in ethanol, even though after the addition of LiI in the solution (Figure S7). Moreover, we found that, when AlI_3 was dissolved in ethanol, the anti-symmetric C-C-O stretch⁵ at 1052 cm^{-1} (Figure S8 b) and the out-of-plane C-C-O deformation⁵ at 436 cm^{-1} (Figure S8 a) shifted to low frequencies. The red-shift of Raman band means that the interaction between the Al^{3+} ions and hydroxyl group. This kind of shift had been observed in other metal ions and alcohols system.⁶

Moreover, it can be explained that the dissociation of AlI_3 in ethanol is due to an interaction between cations and hydroxyl group.

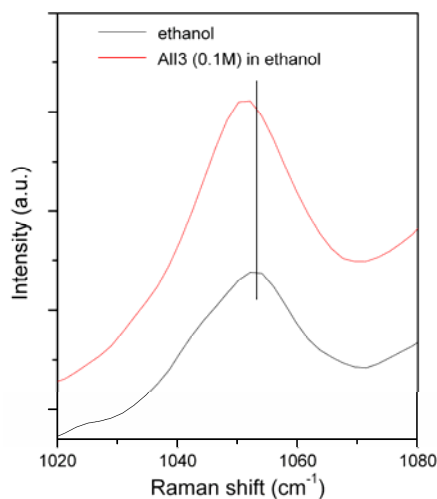
(3) Secondary Ion Mass Spectrometry (SIMS) results

Mass spectrometry is widely used to identify ions species in solutions.⁷ Secondary Ion Mass Spectrometry (SIMS) has the capability of analyzing all elements in the periodic table as well as all isotopes. Typical detection limits for trace elemental analysis are in the ppm to ppb range.⁸ In addition, SIMS was used successfully to detect ions species in an ionic liquid

containing AlCl_4^- , Al_2Cl_7^- and $\text{Al}_2\text{OCl}_5^-$ etc,⁹ which is a quite similar system to the present system.



(a)



(b)

Figure S8 (a) and (b) Raman spectra of ethanol and AlI_3 (0.1 M) ethanol solution to show the shifts of Raman peaks after AlI_3 is dissolved in ethanol. (The straight lines are drawn to indicate the Raman frequencies shifts)

Table S1 Mass spectrum data for saturated AlI_3 ethanol solution

m/z	126.9050	253.8095	267.7995	386.7156
ions	I^-	I_2^-	NaI_2^-	CsI_2^-

The Mass Spectrum (Table S1 and Figure S9) of saturated AlI_3 ethanol solution (ca. 1M) was recorded by

a Bruker APEX II FT-ICR-MS using the Cs^+ ions as the ions source.

Besides the peaks at 267.7995 and 386.7156, which could be ascribed to NaI_2^- and CsI_2^- respectively, the observed ions were I^- and I_2^- . The NaI_2^- peak may cause by the impurity in the commercial AlI_3 (Aldrich, 95%) and the CsI_2^- peak was due to the interaction of Cs^+ and I^- . So from the mass spectra, no AlI_4^- could be observed.

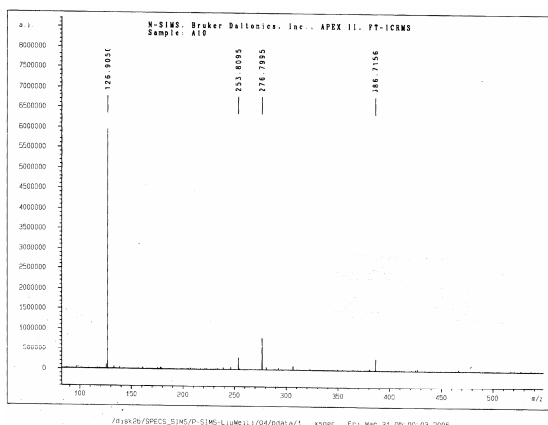


Figure S9 Mass spectra of saturated AlI_3 ethanol solution (ca. 1M)

(4) Ionic conductivity measurement results

Ionic conductivity measurements of electrolytes were carried out by an electrochemical cell of Pt electrodes assembled in the glove box. The cell constant was determined with 0.01 M KCl solution at 25 °C. The ionic conductivities of electrolytes were determined by an AC impedance technique using an HP 4192A impedance analyzer from 5 Hz to 13 MHz. The AC voltage was fixed at 0.005V. The conductivity measurement data were analyzed by ZView.

The conductivities of the *in-situ* prepared AlI_3 (0.1 M, other solutions of AlI_3 used commercial AlI_3), commercial AlI_3 (0.1M) and LiI (0.3M) in ethanol were measured and were listed in Table S2.

Table S2 Ionic conductivities (σ) of AlI_3 and LiI solutions (1)

Solutions (25°C)	In-situ AlI_3 (0.1 M) in ethanol	Commercial AlI_3 (0.1 M) in ethanol	LiI (0.3 M) in ethanol
σ (Scm^{-1})	5.20×10^{-3}	5.12×10^{-3}	3.79×10^{-3}

The conductivities of AlI_3 in n-hexane (0.1 M and 0.5 M), LiI in ethanol solution (0.1 M) and ethanol solution of AlI_3 (0.1 M) and LiI (0.1 M) were also measured to study the conductivity of AlI_3 in n-hexane and ethanol solutions.

Table S3 lists the ionic conductivities of AlI_3 and LiI solutions. Only if AlI_3 dissociates into ions can the AlI_3 solution possess respectable ionic conductivity. The ionic conductivity of AlI_3 (0.1 M) ethanol solution was determined to be $5.12 \times 10^{-3} \text{ Scm}^{-1}$ (Table S2). The high conductivity suggests the dissociation of AlI_3 in ethanol. In contrast, the conductivity of either 0.1M or 0.5M AlI_3 n-hexane solution was in the $10^{-10} \text{ Scm}^{-1}$ magnitude. This is due to the association of AlI_3 as dimmers in n-hexane as mentioned above: no free ions are available in the n-hexane AlI_3 solution.

Table S3 Ionic conductivities (σ) of AlI_3 and LiI solutions (2)

Solutions (25°C)	σ (Scm^{-1})
AlI_3 (0.1 M) in n-hexane	$< 10^{-10}$
AlI_3 (0.5 M) in n-hexane	$< 10^{-10}$
AlI_3 (0.1 M) in ethanol	5.12×10^{-3}
LiI (0.1 M) in ethanol	1.96×10^{-3}
Ethanol solution of AlI_3 (0.1 M) and LiI (0.1M)	7.66×10^{-3}

On the other hand, the conductivity of ethanol solution of AlI_3 (0.1M) and LiI (0.1M) was also measured to investigate the influence of LiI addition on the conductivity of AlI_3 ethanol solution. Since the conductivity of a solution can be written as:

$$\sigma = \sum n_i c_i u_i \quad (1)$$

where n is the valence of a free ion, c is the concentration of the free ion and u is the mobility of the ion. AlI_4^- is much larger than other ions (Al^{3+} , Li^+ , I^-) in the electrolyte, if AlI_4^- ions were formed in the electrolyte, the conductivity would decrease due to the large volume of AlI_4^- and the decreased concentration of free ions in the electrolyte. However, contrary to this prediction, the conductivity of ethanol solution of AlI_3 (0.1M) and LiI (0.1M) was $7.66 \times 10^{-3} \text{ Scm}^{-1}$. This value

is comparable to the sum of individual values of AlI_3 (0.1M) ethanol solution and LiI (0.1M) ethanol solution. So the formation of AlI_4^- is unlikely in the ethanol solution of AlI_3 (0.1M) and LiI (0.1M).

Based on the above analysis and experimental results, we conclude that AlI_3 has different state in different solvents. In inert and non-polar solvents, such as n-hexane (dielectric constant, $\epsilon = 1.89$ at 20°C)¹⁰, it exists as dimer molecules. In polar solvents, such as ethanol ($\epsilon = 25.3$ at 20°C)¹⁰, it dissociates into Al^{3+} ions and I^- ions due to the interaction between cations and ethanol molecules, as confirmed by FT-Raman spectra. In the meantime, AlI_4^- ions could not be detected in the AlI_3 ethanol solutions, even though in the case that excessive I^- ions were present by adding LiI . Actually, the working principle of DSSC is based on the transport of I^- and I_3^- . The high ionic conductivity and the respectable energy conversion efficiency of DSSC achieved by AlI_3 ethanol electrolytes were also means the dissociation of AlI_3 in ethanol.

REFERENCES for Supporting Information:

- (a) Wade, K.; Banister, A. J. In *Comprehensive Inorganic Chemistry*, Bailar, J. C. Jr.; Emeléus, H.J.; Sir Nyholm, R.; Trotman-Dickenson, A.F. Eds.; Pergamon, Oxford, 1973; Vol.3, p1023. (b) Baaz, M. Gutmann, V. In *Friedel-Crafts and Related Reactions*; Olah, G. A. Eds.; Interscience Publishers: New York, 1963; Vol.1, pp367-377.
- (a) Begun, G.M.; Boston, C.R.; Torsi, G.; Mamantov, G. *Inorg. Chem.*, **1971**, 5, 886. (b) Aubauer, C.; Engelhardt, G.; Klapötke, T.M.; Schulz, A. *J. Chem. Soc., Dalton Trans.*, **1999**, 1729.
- Kebede, Z.; Lindquist, S.-E. *Sol. Energy Mat. Solar Cells*, **1999**, 57, 259.
- (a) Wade, K.; Banister, A. J. In *Comprehensive Inorganic Chemistry*, Bailar, J. C. Jr.; Emeléus, H.J.; Sir Nyholm, R.; Trotman-Dickenson, A.F. Eds.; Pergamon, Oxford, 1973; Vol.3, p1015. (b) Beattie, I.R.; Horder, J.R. *J. Chem. Soc. A*, **1969**, 2655. (c) Adams, D.M.; Churchill, R.G. *J. Chem. Soc. A*, **1970**, 697.
- Characteristic Raman Frequencies of Organic Compounds*, Dollish, F.R.; Fateley, W.G.; Bentley, F.F.; John Wiley & Sons, Inc.: New York, London, Sydney, Toronto, 1974; Chap.3.
- (a) Hester, R.E.; Plane, R.A. *Spectrochimica Acta*, **1967**, 23A, 2289. (b) Al-Baldawi, S.A.; Brooker, M.H.; Gough, T.E.; Irish, D.E. *Can. J. Chem.*, **1970**, 48, 1202. (c) Abe, N.; Ito, M. *J. Raman Spectrosc.*, **1978**, 7, 161. (d) Kanno, H.; Yamauchi, S. *J. Raman Spectrosc.*, **1993**, 24, 403.
- (a) Bergeron, D.E.; Roach, P.J.; Castleman, A.W. Jr.; Jones, N.O.; Khanna, S.N. *Science*, **2005**, 307, 231. (b) Abdul-Sada, A.K.; Greenway, A.M.; Seddon K.R. Welton, T. *Org. Mass Spectrom.*, **1992**, 27, 648. (c) Abdul-Sada, A.K.; Greenway, A.M.; Seddon K.R. Welton, T. *Org. Mass Spectrom.*, **1993**, 28, 759. (d) Wicelinski, S.P.; Gale, R.J.; Pamidimukkala, K.M.; Laine, R.A. *Anal. Chem.*, **1988**, 60, 2228. (e) Lee, T. D.; Anderson, W.R. Jr.; Daves, G. D. Jr. *Anal. Chem.*, **1981**, 53, 304.
- (a) Hanton, S.D. *Chem. Rev.*, 2001, 101, 527. (b) Pacholski, M.L.; Winograd, N. *Chem. Rev.*, 1999, 99, 2977. (c) http://www.albanynanotech.org/Programs/metrology/pdf/PHI_6300.pdf
- Franzen, G.; Gilbert, B.P.; Pelzer, G.; DePauw, E. *Org. Mass Spectrom.*, **1986**, 21, 443.
- Lange's Handbook of Chemistry*, Dean, J.A. Ed.; McGraw-Hill Inc., New York, 1998.

Full form of Reference (8):

Nazeeruddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi C. A.; Grätzel, M. *J. Am. Chem. Soc.*, **2001**, 123, 1613.